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(54) Title: CHEMICAL PRODUCT AND METHOD

(57) Abstract: The invention relates to thermally expandable microspheres comprising a thermoplastic polymer shell and a propellant entrapped therein, wherein said polymer shell is made of a homo- or co-polymer from ethylenically unsaturated monomers comprising more than 85 wt% of nitrile containing monomers and said propellant comprises at least 50 wt% of isooctane. The invention further relates to preparation and use of expandable microspheres, a composition comprising expandable microspheres and articles comprising foamed material containing expanded microspheres.

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## CHEMICAL PRODUCT AND METHOD

The present invention relates to expandable thermoplastic microspheres comprising a shell and a propellant entrapped therein, a method of their preparation, use of such microspheres as a foaming agent, expandable compositions comprising such  
5 microspheres, and articles comprising foamed material containing expanded microspheres.

Expandable thermoplastic microspheres comprising a thermoplastic polymer shell and a propellant entrapped therein are commercially available under the trademark Expancel™ and are used as a foaming agent in many different applications, such as in  
10 elastomers, thermoplastic elastomers, polymers, putty, underbody coating, plastisols, printing ink, paper, explosives and cable insulations. Microspheres and their production are also described in detail in, for example, US 3615972, EP 486080 JP 87-286534, WO 99/46320 and WO 99/43758.

In such microspheres, the propellant is normally a liquid having a boiling  
15 temperature not higher than the softening temperature of the thermoplastic polymer shell. Upon heating, the propellant evaporates to increase the internal pressure at the same time as the shell softens, resulting in significant expansion of the microspheres, normally from about 2 to about 5 times their diameter. The temperature at which the expansion starts is called  $T_{start}$ , while the temperature at which maximum expansion is reached is  
20 called  $T_{max}$ . When  $T_{max}$  is exceeded the propellant has been released through the polymer shell to such an extent that the microspheres start to collapse.

It is generally desirable to achieve as high degree of expansion of the microspheres as possible, preferably when included as a foaming agent in thermoplastics, rubber or thermoplastic elastomers. In many applications, for example  
25 when included in compositions to be worked at high temperature without risk for unintentional expansion, it is also desirable that  $T_{start}$  is comparatively high. In many cases it is also advantageous with a high  $T_{max}$  as the start of collapse of the microspheres during expansion then occurs later.

Thus, it is an object of the present invention to provide thermally expandable  
30 microspheres with high values for  $T_{start}$  and  $T_{max}$ , and high expansion capability at high temperatures.

It is another object of the invention to provide expandable compositions including thermally expandable microspheres, which compositions can be worked at a comparatively high temperature without unintentional expansion.

35 It is still another object of the invention to provide foamed materials containing expanded microspheres.

It has been found that these objects can be achieved by microspheres as defined in the appended claims.

More specifically, the invention concerns thermally expandable microspheres comprising a thermoplastic polymer shell and a propellant entrapped therein, wherein  
5 said polymer shell is made of a homo- or co-polymer from ethylenically unsaturated monomers comprising more than 85 wt%, preferably more than 92 wt%, more preferably more than 95 wt%, most preferably more than 98 wt% of nitrile containing monomers, or even substantially consisting of nitrile containing monomers, while said propellant comprises at least, suitably more than 50 wt%, preferably more than 55 wt%, more  
10 preferably more than about 60 wt% most preferably more than about 70 wt% of isooctane, or even substantially consists of isooctane. The term isooctane as used herein refers to 2,2,4-trimethyl pentane.

Preferably  $T_{\text{start}}$  is within the range from about 80 to about 200°C, more preferably from about 115 to about 200°C, most preferably from about 130 to about  
15 200°C, while  $T_{\text{max}}$  preferably is higher than 190°C, most preferably higher than 200°C. Normally  $T_{\text{max}}$  does not exceed 300°C. The microsphere bulk density after heating to 220°C is preferably lower than 15 g/l, most preferably lower than 12 g/l.

The nitrile containing monomers used for the polymer shell are preferably mainly selected from one or more of acrylo nitrile, methacrylo nitrile,  $\alpha$ -chloroacrylo nitrile,  $\alpha$ -ethoxyacrylo nitrile, fumaro nitrile, croto nitrile, most preferably acrylo nitrile, methacrylo  
20 nitrile or a mixture thereof. If other ethylenically unsaturated monomers are present, preferably in an amount from 0 to about 5 wt%, most preferably from 0 to about 2 wt%, they are preferably selected from one or more of acrylic esters such as methylacrylate or ethyl acrylate, methacrylic esters such as methyl methacrylate, isobornyl methacrylate or  
25 ethyl methacrylate, vinyl chloride, vinylidene chloride, vinyl pyridine, vinyl esters such as vinyl acetate, styrenes such as styrene, halogenated styrenes or  $\alpha$ -methyl styrene, butadiene, isoprene, chloroprene. The softening temperature of the polymer shell, in most cases essentially corresponding to its glass transition temperature ( $T_g$ ), is preferably within the range from about 80 to about 200°C, more preferably from about 115 to about  
30 200°C most preferably from about 130 to about 200°C. Preferably the polymer shell constitutes from about 70 to about 90 wt%, most preferably from about 75 to about 85 wt% of the total microsphere.

It may sometimes be desirable that the monomers for the polymer shell also comprise crosslinking multifunctional monomers, such as one or more of divinyl benzene,  
35 ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, glycerol di(meth)acrylate, 1,3-butanediol di(meth)acrylate,

neopentyl glycol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, pentaerythritol hexa(meth)acrylate, dimethylol tricyclodecane di(meth)acrylate, triallylformal tri(meth)acrylate, allyl methacrylate, trimethylol propane tri(meth)acrylate, trimethylol propane triacrylate, 5 tributanediol di(meth)acrylate, PEG #200 di(meth)acrylate, PEG #400 di(meth)acrylate, PEG #600 di(meth)acrylate, 3-acryloyloxyglycol monoacrylate, triacryl formal or triallyl isocyanate. If present, such crosslinking monomers preferably constitutes from about 0.1 to about 1 wt%, most preferably from about 0.2 to about 0.5 wt% of the total amounts of monomers for the polymer shell.

10 The propellant may, apart from isooctane, comprise up to totally 50 wt% of one or more of butanes, pentanes, hexanes, heptanes, petroleum distillates or other liquids with a suitable boiling point or boiling point range. Particularly preferred hydrocarbons for use in combination with isooctane are isobutane, isopentane, n-pentane, n-hexane, petroleum ether and n-heptane. Suitably the propellant is liquid at room temperature and 15 has a boiling point at atmospheric pressure below the softening point of the polymer shell. Preferably the boiling point at atmospheric pressure is within the range from about -20 to about 150°C, most preferably from about 20 to about 100°C. It is particularly preferred that the propellant has a boiling point or boiling point range so a temperature above 50°C, more preferably above 60°C, most preferably above 70°C, but preferably not higher than 20 about 150°C, would be required to evaporate at least 50 wt%, preferably at least 80 wt% of the propellant at atmospheric pressure. Preferably the propellant constitutes from about 10 to about 30 wt%, most preferably from about 15 to about 25 wt% of the total 25 microsphere.

Apart from the polymer shell and the propellant the microspheres may comprise 25 further substances added during the production thereof, normally in an amount from about 1 to about 20 wt%, preferably from about 2 to about 10 wt%. Examples of such substances are solid suspending agents, such as one or more of silica, chalk, bentonite, starch, crosslinked polymers, methyl cellulose, gum agar, hydroxypropyl methylcellulose, carboxy methylcellulose, colloidal clays, and/or one or more salts, oxides or hydroxides of 30 metals like Al, Ca, Mg, Ba, Fe, Zn, Ni and Mn, for example one or more of calcium phosphate, calcium carbonate, magnesium hydroxide, barium sulphate, calcium oxalate, and hydroxides of aluminium, iron, zinc, nickel or manganese. If present, these solid suspending agents are normally mainly located to the outer surface of the polymer shell. Even if a suspending agent has been added during the production of the microspheres, 35 this may have been washed off at a later stage and could thus be substantially absent from the final product.

The average particle size of the expandable microspheres is suitably from about 1 to about 500  $\mu\text{m}$ , preferably from about 1 to about 200  $\mu\text{m}$ , most preferably from about 3 to about 100  $\mu\text{m}$ , most preferably from about 5 to about 50  $\mu\text{m}$ . By heating to a temperature above  $T_{\text{start}}$ , it is normally possible to expand the microspheres from about 2  
5 to about 7 times, preferably from about 4 to about 7 times, their diameter

The invention further concerns a process for producing thermally expandable microspheres as described above, comprising the steps of polymerising ethylenically unsaturated monomers in an aqueous suspension in the presence of a propellant to yield microspheres comprising a homo- or co-polymer shell entrapping said propellant,  
10 wherein said ethylenically unsaturated monomers comprises more than 85 wt%, preferably more than 92 wt%, more preferably more than 95 wt%, most preferably more than 98 wt% of nitrile containing monomers, particularly most preferably substantially consists of nitrile containing monomers, while said propellant comprises at least, suitably more than 50 wt%, preferably more than 55 wt%, more preferably more than about 60  
15 wt% most preferably more than about 70 wt% of isooctane, particularly most preferably substantially consists of isooctane.

Regarding preferred monomers, propellants and other features of the final product, the above description of the novel microspheres is referred to.

In applicable parts, the polymerisation may be conducted as described in the  
20 earlier mentioned patent publications regarding microspheres.

In a suitable, preferably batchwise procedure for preparing microspheres of the invention the polymerisation is conducted in a reaction vessel as described below. For 100 parts of monomer phase (suitably including monomers and propellant), one or more polymerisation initiator, preferably in an amount from about 0.1 to about 5 parts, aqueous  
25 phase, preferably in an amount from about 100 to about 800 parts, and one or more preferably solid colloidal suspending agent, preferably in an amount from about 1 to about 20 parts, are mixed and homogenised. The temperature is suitably set from about 40 to about 90°C, preferably from about 50 to about 80°C, while the suitable pH depends on the suspending agent used. For example, alkaline pH, preferably from about 7 to about 12, most preferably from about 8 to about 10, is suitable if the suspending agent is  
30 selected from salts, oxides or hydroxides of metals like Al, Ca, Mg, Ba, Fe, Zn, Ni and Mn, for example one or more of calcium phosphate, calcium carbonate, chalk, magnesium hydroxide, barium sulphate, calcium oxalate, and hydroxides of aluminium, iron, zinc, nickel or manganese, each one of these agents having different optimal pH  
35 depending on solubility data. Acidic pH, preferably from about 1 to about 6, most preferably from about 3 to about 5, is suitable if the suspending agent is selected from

silica, bentonite, starch, methyl cellulose, gum agar, hydroxypropyl methylcellulose, carboxy methylcellulose, colloidal clays.

In order to enhance the effect of the suspending agent, it is also possible to add small amounts of one or more promoters, for example from about 0.001 to about 1 wt%.

- 5 Usually, such promoters are organic materials and may, for example, be selected from one or more of water-soluble sulfonated polystyrenes, alginates carboxymethylcellulose, tetramethyl ammonium hydroxide or chloride or water-soluble complex resinous amine condensation products such as the water-soluble condensation products of diethanolamine and adipic acid, the water-soluble condensation products of ethylene  
10 oxide, urea and formaldehyde, polyethylenimine, amphoteric materials such as proteinaceous, materials like gelatin, glue, casein, albumin, gluten and the like, non-ionic materials like methoxycellulose, ionic materials normally classed as emulsifiers, such as soaps, alkyl sulfates and sulfonates and the long chain quaternary ammonium compounds.

- 15 Conventional radical polymerisation may be used and initiators are suitably selected from one or more of organic peroxides such as dialkyl peroxides, diacyl peroxides, peroxy esters, peroxy dicarbonates, or azo compounds. Suitable initiators include dicetyl peroxy dicarbonate, tert-butyl cyclohexyl peroxy dicarbonate, dioctanyl peroxide, dibenzoyl peroxide, dilauroyl peroxide, didecanoyl peroxide, tert-butyl  
20 peracetate, tert-butyl perlaurate, tert-butyl perbenzoate, tert-butyl hydroperoxide, cumene hydroperoxide, cumene ethylperoxide, diisopropyl hydroxy dicarboxylate, azo-bis dimethyl valeronitrile, azo-bis isobutyronitrile, azo-bis (cyclo hexyl carbo nitrile) and the like. It is also possible to initiate the polymerisation with radiation, such as high energy ionising radiation.

- 25 When the polymerisation is complete, microspheres are normally obtained as an aqueous slurry, which can be dewatered by any conventional means, such as bed filtering, filter pressing, leaf filtering, rotary filtering, belt filtering and centrifuging, and then dried by any conventional means, such as spray drying, shelf drying, tunnel drying, rotary drying, drum drying, pneumatic drying, turbo shelf drying, disc drying and fluidised bed-  
30 drying.

- The invention further concerns use of thermally expandable microspheres as described above as a foaming agent, particularly in materials like plastics, rubber and paint that have to be excerpted to high temperatures for processing before they are supposed to foam, which temperatures, for example, may be above about 115°C,  
35 particularly above about 130°C. The amount of micro spheres is preferably from about 0.1 to about 30 wt%, most preferably from about 0.5 to about 20 wt%. Examples of materials in which the novel microspheres advantageously are included are polyethylene,

polypropylene, polystyrene, ABS (acrylonitrile butadiene styrene), which may be used for low weight high temperature processed products. Other examples include rubber for the tread surface of tyres, particularly of crude rubber and/or SBR (styrene butadiene rubber), or rubber for soles for shoes, particularly of TPU (thermoplastic uretanes), SBS (styrene butadiene styrene) and/or SEBS (styrene ethylene butadiene styrene), or paint intended to be applied by high pressure.

Moreover, the invention concerns an expandable composition comprising thermally expandable microspheres as described above as a foaming agent, preferably in an amount from about 0.1 to about 30 wt%, most preferably from about 0.5 to about 20 wt%. The composition suitably further comprise one or more polymeric substances, for example an amount from about 70 to about 99.9 wt%, most preferably from about 80 to about 99.5 wt%, which polymeric substances may include one or more of polyethylene, polypropylene, polystyrene, ABS, SBS, SEBS, crude rubber, SBR, TPU or similar materials.

Finally, the invention concerns articles comprising a foamed material containing expanded microspheres obtainable by heating expandable microspheres as described above, preferably when included in a composition as described above. Examples of such articles are rubber tyres, soles for shoes and low weight high temperature processed products. The expandable microspheres have suitably been heated to a temperature from about 140 to about 260°C, preferably from about 140 to about 240°C, most preferably from about 150 to about 230°C, resulting in an increase in volume and decrease in density of the foamed material.

The invention will now be further described in connection with the following Examples, which, however, not should be interpreted as limiting the scope thereof. If not otherwise stated, all parts and percentages refer parts and percent by weight.

Example 1: A dispersion of 7 parts of  $Mg(OH)_2$  and 340 parts of water was prepared. A mixture of 2 parts of initiator, 60-65 parts of acrylo nitrile, 30-35 parts of methacrylo nitrile and 0.5-5.5 parts of one or two of a monofunctional, difunctional or trifunctional methacrylate monomer (given in table 1) and 21 parts of propellant (given in table 1) was added to form a reaction mixture, which then was homogenised to a suitable monomer droplet size. The initiator was one of dilauroyl peroxide (denoted I in table 1) or 2,2'-azobis(isobutyronitrile) (denoted II in table 1). After homogenization, the mixture was transferred to a 300 ml bottle which was sealed and heated while agitating the mixture during polymerisation. After 15 - 20 hours at 60-65 °C the microspheres obtained were filtered, washed and dried. Expansion of the microspheres was measured in a temperature ramping experiment in a Mettler-Toledo Thermomechanical Analyser. The

results are shown in Table 1. It appears that when at least 50 wt% isooctane is used as propellant both high  $T_{start}$  and low density at high temperature (220°C) could be obtained.

Table 1

Propellant	Initiator	Methacrylate monomers	Nitrile containing monomers (wt%)	T <sub>start</sub> (°C)	T <sub>max</sub> (°C)	Bulk density at 220°C (g/l)
100% IP	I	TMPTMA	99.5%	111	190	22.0
100% IP	I	EGDMA	99.5%	110	192	12.7
100% IP	I	BDDM	99.5%	111	188	23.1
100% NP	I	TMPTMA	99.5%	112	185	35.0
100% NP	I	EGDMA	99.5%	117	182	60.7
100% NP	I	BDDM	99.5%	117	184	40.8
100% SBP 60/95	I	TMPTMA	99.5%	128	197	16.0
100% SBP 60/95	II	TMPTMA	99.5%	155	195	17.2
100% SBP 60/95	I	EGDMA	99.5%	127	197	22.1
100% SBP 60/95	I	BDDM	99.5%	137	197	17.8
100% NH	I	TMPTMA	99.5%	177	213	30.0
100% NH	I	EGDMA	99.5%	152	217	13.3
100% NH	I	BDDM	99.5%	148	215	14.3
100% NO	I	TMPTMA	99.5%	204	212	58.0
100% NO	I	EGDMA	99.5%	197	212	65.2
100% NO	I	BDDM	99.5%	206	221	44.8
100% IO	I	TMPTMA	99.5%	178	216	11.0
100% IO	II	TMPTMA	99.5%	179	203	10.5
100% IO	I	EGDMA	99.5%	145	218	10.4
100% IO	I	BDDM	99.5%	155	218	8.2
100% IO	I	TMPTMA, MMA	97.5%	148	217	14
100% IO	I	TMPTMA, MMA	94.5%	147	217	13
100% IO	I	BDDM, MMA	94.5%	158	219	11
100% IO	I	BDDM, FMA	94.5%	175	218	12.6
100% IO	I	TMPTMA, EMA	94.5%	169	218	12.8
100% IO	I	EGDMA, MMA	94.5%	159	218	16.3
100% IO	I	EGDMA, EMA	94.5%	156	219	16.5
90% IO, 10% IP	I	TMPTMA	99.5%	149	211	9
90% IO, 10% NP	I	TMPTMA	99.5%	151	211	9
83% IO, 17% SBP 60/95	I	TMPTMA	99.5%	173	212	12
83% IO, 17% SBP 60/95	I	EGDMA	99.5%	144	215	11
83% IO, 17% SBP 60/95	I	BDDM	99.5%	145	215	10
83% IO, 17% IP	I	TMPTMA	99.5%	140	203	10
83% IO, 17% IP	I	EGDMA	99.5%	134	204	10
83% IO, 17% IP	I	BDDM	99.5%	128	205	10
67% IO, 33% SBP 60/95	I	TMPTMA	99.5%	157	208	12
67% IO, 33% SBP 60/95	I	EGDMA	99.5%	138	212	13
67% IO, 33% IP	I	TMPTMA	99.5%	128	198	12
67% IO, 33% IP	I	EGDMA	99.5%	123	195	11
67% IO, 33% IP	I	BDDM	99.5%	124	199	10
67% IO, 33% NP	I	TMPTMA	99.5%	133	197	9
50% IO, 50% SBP 60/95	I	TMPTMA	99.5%	153	205	14
50% IO, 50% SBP	I	EGDMA	99.5%	137	208	16

Propellant	Initiator	Methacrylate monomers	Nitrile containing monomers (wt%)	Tstart (°C)	Tmax (°C)	Bulk density at 220°C (g/l)
60/95						
50% IO, 50% SBP 60/95	I	BDDM	99.5%	135	208	12
50% IO, 50% IP	I	TMPTMA	99.5%	118	191	15
50% IO, 50% IP	I	EGDMA	99.5%	117	192	12
50% IO, 50% IP	I	BDDM	99.5%	116	198	11
50% IO, 50% NP	I	TMPTMA	99.5%	131	194	11

IO=isooctane; IP=isopentane; NP=n-pentane; SBP 60/95= petroleum destillate with boiling point range of 60-95°C; NH=n-heptane; NO=n-octane; MMA=methyl methacrylate; EMA=ethyl methacrylate; TMPTMA=trimethylolpropane trimethacrylate; EGDMA=ethylene glycol dimethacrylate; BDDM= butane diol dimethacrylate

5

Example 2: Microspheres prepared in Example 1 with a polymer shell made from 99.5% nitrile containing monomers and 100% isooctane as propellant were mixed into SBS thermoplastic rubber in a total amount of 2.75 wt%. The microsphere containing rubber mixture was injection moulded with a barrel temperature of 210-225°C and an injection speed of 70-150 mm/s to square-shaped plates. The density of the plates was measured, and found to be lowered from 996 g/l to 729 g/l by introducing the microspheres.

As a comparison, this experiment was repeated with microspheres with a polymer shell made from 99.5% nitrile containing monomers and 100% isopentane as propellant. The density of the plates was found to be lowered from 996 g/l to 857 g/l by introducing the microspheres. Furthermore, a discoloration of the material was found in comparison to the material containing isooctane.

9  
CLAIMS

1. Thermally expandable microspheres comprising a thermoplastic polymer shell and a propellant entrapped therein, c h a r a c t e r i s e d in that said polymer shell is made of a homo- or co-polymer from ethylenically unsaturated monomers comprising  
5 more than 85 wt% nitrile containing monomers and said propellant comprises at least 50 wt% isooctane.

2. Microspheres as claimed in claim 1, wherein said ethylenically unsaturated monomers comprise more than 92 wt% nitrile containing monomers.

3. Microspheres as claimed in claim 2, wherein said ethylenically unsaturated  
10 monomers comprise more than 98 wt% nitrile containing monomers.

4. Microspheres as claimed in any one of the claims 1-3, wherein said nitrile containing monomers mainly are selected from acrylo nitrile, methacrylo nitrile or a mixture thereof.

5. Microspheres as claimed in any one of the claims 1-4, wherein the softening  
15 temperature of said polymer shell is within the range from about 80 to about 200°C.

6. Microspheres as claimed in any one of the claims 1-5, wherein said propellant comprises more than about 60 wt% of isooctane.

7. Microspheres as claimed in claim 6, wherein said propellant comprises more than about 70 wt% of isooctane.

20 8. Microspheres as claimed in any one of the claims 1-6, wherein said propellant comprises isooctane and one or more of isobutane, isopentane, n-pentane, n-hexane, petroleum ether and n-heptane.

9. Microspheres as claimed in any one of the claims 1-8, wherein said propellant has a boiling point or boiling point range so a temperature above 50°C would be required  
25 to evaporate at least 50 wt% of the propellant at atmospheric pressure.

10. Process for producing thermally expandable microspheres according to any one of the claims 1-9, comprising the steps of polymerising ethylenically unsaturated monomers in an aqueous suspension in the presence of a propellant to yield microspheres comprising a hollow homo- or co-polymer shell entrapping said propellant,  
30 c h a r a c t e r i s e d in that said ethylenically unsaturated monomers comprises more than 85 wt% of nitrile containing monomers and said propellant comprises more than 50 wt% of isooctane.

11. Use of thermally expandable microspheres according to any one of the claims 1-9 as a foaming agent.

35 12. Expandable composition comprising one or more polymeric substances and thermally expandable microspheres according to any one of the claims 1-9 as a foaming agent.

13. An article comprising foamed material containing expanded microspheres obtainable by heating expandable microspheres according to any one of the claims 1-9.

## INTERNATIONAL SEARCH REPORT

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 PCT/SE 01/00683

 A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 B01J13/02 B01J13/14 B01J13/18

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 486 080 A (CASCO NOBEL AB) 20 May 1992 (1992-05-20) cited in the application column 4, line 5 -column 4, line 41	1-13
A	GB 989 264 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 14 April 1965 (1965-04-14) example 16	1-13
A	US 3 787 327 A (EMRICK D) 22 January 1974 (1974-01-22) examples 1-9	1-13

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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